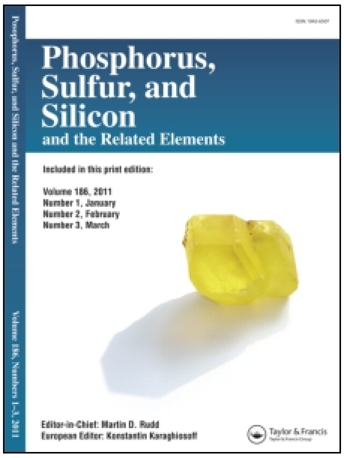

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SOME REACTIONS OF 2-CYANOMETHYLBENZOTHIAZOLE VERSUS THE CORRESPONDING BENZIMIDAZOLE DERIVATIVE

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To cite this Article Nawwar, Galal A. M. , Zaki, Magdi M. E. A. and Chabaka, Laila M.(1993) 'SOME REACTIONS OF 2-CYANOMETHYLBENZOTHIAZOLE VERSUS THE CORRESPONDING BENZIMIDAZOLE DERIVATIVE', Phosphorus, Sulfur, and Silicon and the Related Elements, 79: 1, 195 — 205

To link to this Article: DOI: 10.1080/10426509308034413

URL: http://dx.doi.org/10.1080/10426509308034413

Phosphorus, Sulfur, and Silicon, 1993, Vol. 79, pp. 195–205
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SOME REACTIONS OF 2-CYANOMETHYLBENZOTHIAZOLE VERSUS THE CORRESPONDING BENZIMIDAZOLE DERIVATIVE

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(Received June 11, 1992; in final form January 1, 1993)

Simple synthesis of several 2-substituted heteroaryl benzoazoles was achieved starting with the conveniently available 2-cyanomethylbenzoazoles (1a,b) via addition, acylation and condensation reactions of (1a,b) followed by cyclization of the obtained polyfunctionally substituted materials which were found to be dependent on the nature of the variable heteroatom.

Key words: 2-cyanomethylbenzothiazole; oxazine rearrangement; benzothiazole by heterocycles; 2-cyanomethylbenzimidazole.

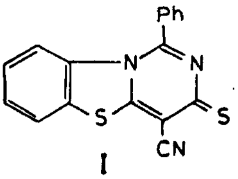
INTRODUCTION

Several 2-substituted heterocyclic benzothiazoles and benzimidazoles are reported to possess herbicidal or anti-fungal activity.[1,2] Recently, we have been involved in a program aiming to explore the synthetic potentials of activated nitriles in the preparation of heterocycles for biological activity evaluation.[3–5] In this investigation, 2-cyanomethylbenzoazoles (1) are the precursors of choice for the preparation of 2-substituted heteroarylbenzoazoles with anticipated biological activity.

RESULTS AND DISCUSSION

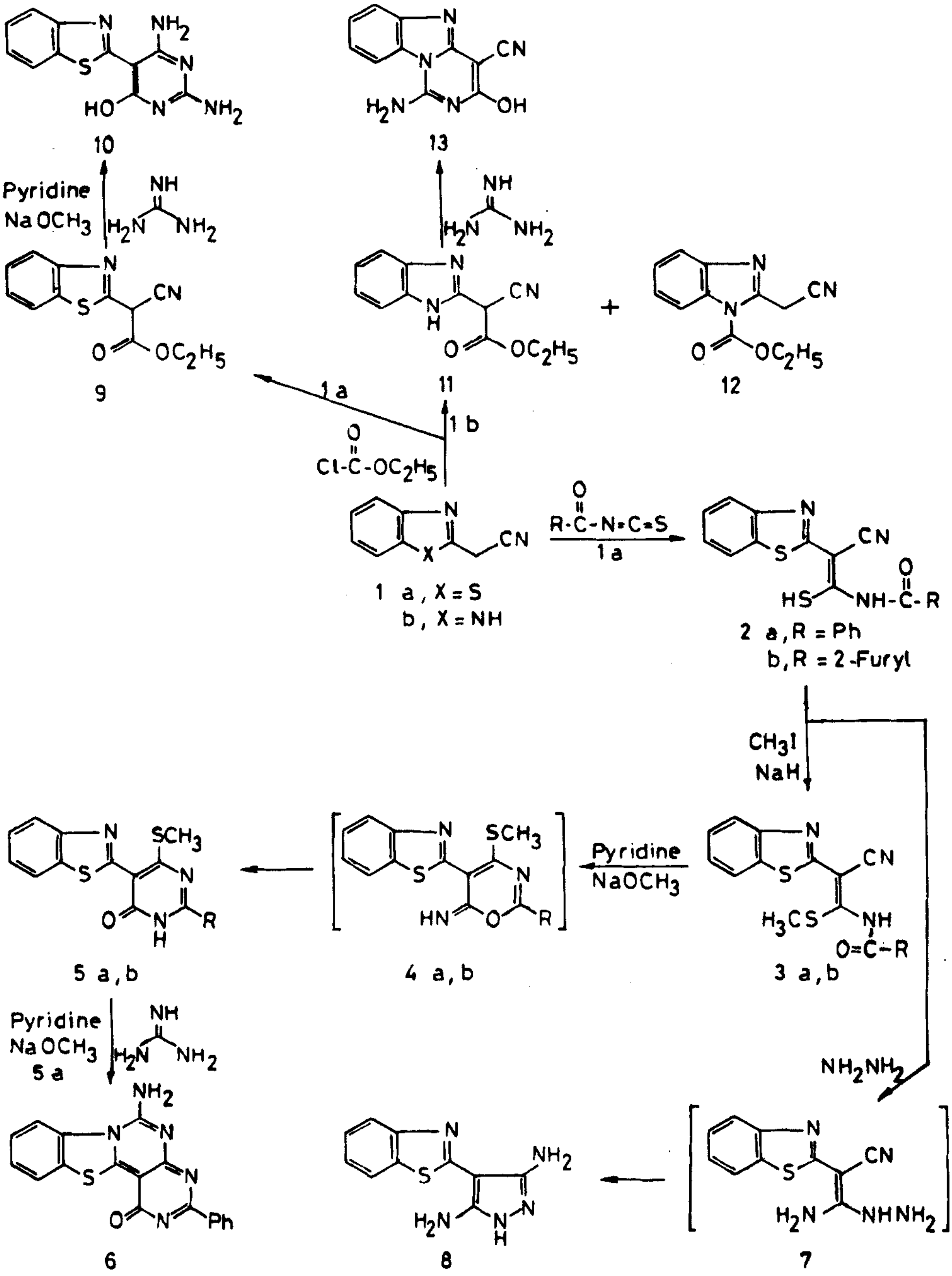
It has been found that (1a) reacts with benzolyisothiocyanate in dioxane at 25°C to yield the 1:1 adduct (2a). Structure (2a) was postulated on the basis of its elemental analysis, IR, M.S. and ^{1}HNMR spectra. The latter showed aromatic protons only along with the (D_2O) exchangeable protons NH and SH.

On boiling the 1,1-adduct (2a) in pyridine to prepare the previously reported pyrimido [6,1-b]benzothiazole I,[6] the starting material (2a) was obtained recovered unchanged.



I

Compound (2a) could be methylated with methyl iodide in the presence of NaH to afford the methylmercapto derivative (3a).



Scheme I

Similar to the behaviour of (1a) towards benzoylisothiocyanate, it also reacted with 2-furoylisothiocyanate giving the 1:1 adduct (2b) which could be also methylated to (3b) under the same reaction conditions used for (2b).

When compound (3a) was boiled under reflux in pyridine in the presence of sodium methoxide, a product of a molecular formula $C_{18}H_{13}N_3OS_2$ (m/z = 351) was obtained. The IR of this product showed carbonyl group absorption at 1660 cm^{-1}; its ^{1}HNMR revealed a singlet at δ 3.9 ppm integrated to 3 protons along with the phenyl and benzothiazole aromatic protons in their expected locations (cf. Table II). These data and elemental analyses could be interpreted for the 2-(pyrimidyl)benzothiazole structure (5a).

An analogous result was obtained with the adduct (3b) and the 2-(pyrimidyl)benzothiazole (5b) was obtained in good yield. Structure (5b) was established from its analytical and spectral data (cf. Tables I and II).

The formation of (5) is assumed to proceed via initial formation of the 2-(oxazinyl) benzothiazole intermediate (4) which rearranged in basic medium to afford the final isolable product (5). A similar assumption has been previously reported.[7] Compound (5a) reacted with guanidine sulfate in pyridine/NaOMe affording the pyrimido[6,1-b]benzothiazole derivative (6) in satisfactory yield. Elemental and spectral data were in agreement with structure (6) (cf. Tables I and II).

Although, the adducts (2a,b) behaved differently towards alkylation with methyl iodide when compared with their benzimidazole analogues, their behaviour towards hydrazine hydrate was found to be parallel.[4]

Thus, when the adduct (3a) reacted with hydrazine hydrate in butanol, a product with a molecular formula $C_{10}H_9N_5S$ (m/z = 231) was obtained. Structure (8) was suggested for this product based on its spectral data (cf. Table II). The formation of (8) from (3a) is assumed to proceed via debenzoylation and replacement of the SCH_3 group both with hydrazine hydrate, to give the intermediate (7) which then cyclized involving the cyano group affording the final isolable product (8).

In agreement with this view, compound (8) was also obtained when the adduct (3b) reacted with hydrazine hydrate under the same experimental conditions used for (3a).

Compound (1a) could be acylated with ethyl chloroformate in the presence of triethylamine to afford the α-carboethoxy derivative (9). The latter reacted with guanidine sulfate in pyridine in presence of sodium methoxide affording the 2-(diaminopyrimidyl)benzothiazole (10) based on spectral and microanalytical data (cf. Tables I and II).

2-Cyanomethylbenzimidazole also reacted with ethyl chloroformate under similar reaction conditions to those used with (1a) but two products were obtained and separated by fractional crystallization. They were identified as the N- and C-acyl derivatives (12) and (11), respectively. When the latter was allowed to react with guanidine sulphate, it behaved differently from its benzothiazole analogue (9) and the reaction afforded the pyrimidobenzimidazole (13). The IR spectrum of (13) revealed a cyano group absorption at σ 2200 cm^{-1} and showed a molecular formula compatible with $C_{11}H_7N_5O$ (m/z = 225).

Following the known approach for the pyridine synthesis,[8] compound (1a) reacted with the propenones (14a,b) in ethanol in presence of 8 equivalents of ammonium acetate to give the 2-(2-aminopyrid-3-yl)benzothiazoles (17a,b), respectively. Structure of compounds (17a,b) was suggested on the basis of their analytical and spectral data (cf. Tables I and II).

In contrast, 2-cyanomethylbenzimidazole (1b) reacted with the propenones (14a,b)

TABLE I

Physical and chemical data for (2a,b; 3a,b; 5a,b; 9; 10; and 11)

Compound No.	**Yield %**	**Solvent/ M.p. °C**	**Molecular formula/ M.wt.**	**Analysis % Calc. / Found**			
				C	**H**	**N**	**S**
2a	80	dioxane	$C_{17}H_{11}N_3OS_2$	60.05	3.29	12.45	19.01
		185	337.407	60.00	3.13	12.24	18.78
2b	75	dioxane	$C_{15}H_9N_3O_2S_2$	55.03	2.77	12.84	19.59
		163	327.371	54.93	2.61	12.35	19.19
3a	70	EtOH	$C_{18}H_{13}N_3OS_2$	61.51	3.73	11.96	18.25
		174	351.433	61.25	3.42	11.80	17.93
3b	72	EtOH	$C_{16}H_{11}N_3O_2S_2$	56.29	3.25	12.31	18.78
		158	341.397	56.08	3.09	12.08	18.38
5a	43	pyridine	$C_{18}H_{13}N_3OS_2$	61.51	3.72	11.95	18.24
		254	351.433	61.33	3.51	11.60	17.88
5b	50	pyridine	$C_{16}H_{11}N_3O_2S_2$	56.29	3.25	12.31	18.78
		246	341.397	56.15	3.20	12.09	18.43
9	85	dioxane	$C_{12}H_{10}N_2O_2S$	58.52	4.09	11.37	13.02
		215	246.278	58.29	3.85	11.09	12.82
10	64	D.M.F./H_2O	$C_{11}H_9N_5OS$	50.95	3.50	27.01	12.37
		283	259.281	50.73	3.31	26.81	12.09
11	50	dioxane	$C_{12}H_{11}N_3O_2$	62.87	4.83	18.33	-
		185	229.23	62.66	4.59	18.00	-

12	20	dioxane/H_2O	$C_{12}H_{11}N_3O_2$	62.87	4.83	18.33	-	-
		164	229.23	62.70	4.57	17.98	-	-
13	40	D.M.F	$C_{11}H_7N_5O$	58.66	3.13	31.10	-	-
		> 300	225.206	58.41	3.00	30.74	-	-
17a	80	dioxane	$C_{20}H_{13}N_3OS_2$	63.97	3.48	11.19	17.07	-
		212	375.44	63.68	3.35	10.87	16.75	-
17b	75	dioxane	$C_{28}H_{18}N_3SCl$	72.48	3.90	9.05	6.91	7.64
		241-43	463.957	72.20	3.65	8.81	6.50	7.23
19a	60	toluene	$C_{20}H_{15}N_3O_2S$	66.46	4.18	11.62	8.87	-
		283	361.404	66.25	3.91	11.25	8.54	-
19b	55	toluene	$C_{28}H_{20}N_3OCl$	74.74	4.48	9.33	-	7.87
		> 300	449.913	74.52	4.26	9.00	-	7.48
20b	70	ethanol	$C_{18}H_{13}N_3$	79.68	4.82	15.48	-	-
		214	271.30	79.44	4.65	15.14	-	-
23	45	D.M.S.O./H_2O	$C_{19}H_{10}N_4S_2$	63.66	2.81	15.63	17.88	-
		269-71	358.42	63.32	2.64	15.27	17.49	-
25	60	D.M.F.	$C_{19}H_{12}N_6$	70.35	3.73	25.91	-	-
		> 300	324.34	70.11	3.49	25.48	-	-

TABLE II

Comp. No.	IR (cm^{-1})	^{1}HNMR (ppm)
2a	3500-3420 (SH and NH), 2200 (CN), 1650 (CO)	2.3 (s, 1H, SH), 7.6 (m, 5H, C_6H_5) 8.1-8.3 (m, 4H, benzothiazole protons).
2b	3480-3300 (SH and NH), 2200 (CN), 1650 (CO)	2.3 (s, 1H, SH), 7.1 (m, 2H, furan H-3, H-4), 7.7-8.3 (m, 5H, furan H-5 and benzothiazole protons).
3a	3400 (NH), 2200 (CN), 1650 (CO)	3.8 (s, 1H, CHCN), 4.2 (s, 3H, SCH_3), 7.4-7.5 (m, 5H, C_6H_5), 7.8 (m, 3H, benzothiazole H-4, H-5 and H-6), 8.1 (m, 1H, benzothiazole H-7).
3b	3400 (NH), 2200 (CN), 1650 (CO)	---
5a	3450 (OH and NH), 1660 (CO)	3.9 (s, 3H, SCH_3), 7.3-7.9 (m, 9H, C_6H_5 and benzothiazole protons).
5b	3450-3250 (OH and NH), 1660 (CO)	4.0 (s, 3H, SCH_3), 7.1-7.9 (m, 7H, furan and benzothiazole protons).
6	3220-3000 (NH_2), 1720 (CO)	1.1-1.3 (m, 2H, NH_2), 7.4-8.1 (m, 9H, C_6H_5 and benzothiazole protons).
8	3380-3200 ($2NH_2$ and NH)	7.9-8.2 (m, 4H, benzothiazole protons,), 11.0 (s, 1H, NH).
9	2200 (CN), 1747 (CO)	1.1 (t, 3H, CH_3), 4.2 (q, 2H, CH_2), 6.0 (s, 1H, CO-CH-CN), 7.2-8.0 (m, 4H, benzothiazole protons).
10	3450-3300 ($2NH_2$), 1660 (CO)	1.0-1.2 (m, 4H, $2NH_2$), 7.1-7.8 (m, 4H, benzothiazole protons).
11	3500-3350 (OH and NH_2), 2200 (CN), 1725 (CO)	1.1-1.2 (t, 3H, CH_3), 4.2 (q, 2H, CH_2), 7.4-8.1 (m, 4H, ArH), 11.2 (brs, 1H, NH), 11.8 (s, 1H, OH).
12	2200 (CN)	1.1 (t, 3H, CH_3), 4.2 (q, 2H, CH_2), 4.5 (s, 2H, CH_2CN), 7.4-7.7 (m, 4H, ArH).
13	3600-3400 (OH and NH_2) 2220 (CN)	7.6-8.1 (m, 4H, ArH), 11.2 (brs, 2H, NH_2), 12.3 (s, 1H, OH).
17a	3800-3730 (NH_2)	4.0 (brs, 2H, NH_2), 7.1-8.1 (m, 10H, benzothiazole, furan and thiophene protons), 8.3 (s, 1H, pyridine H-5).

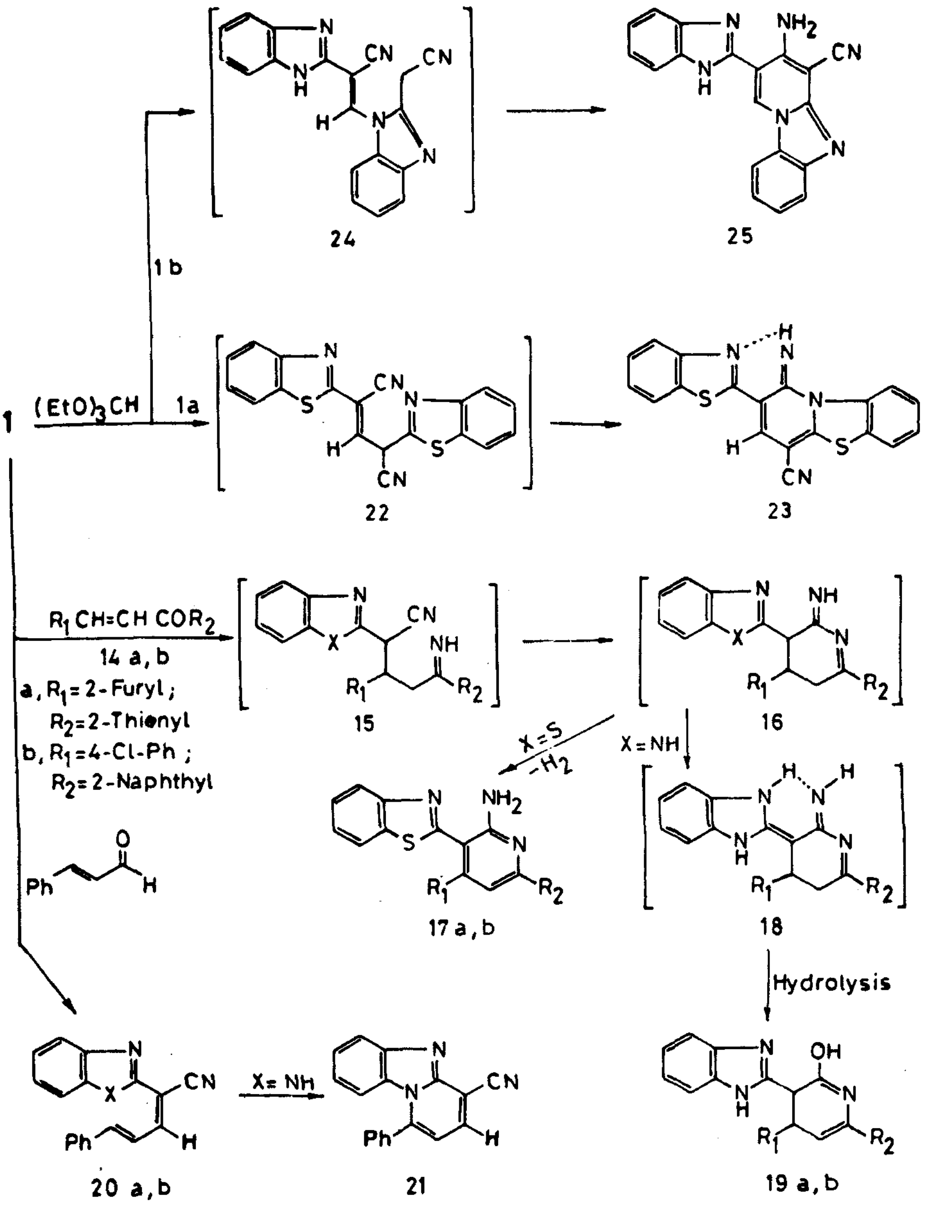
TABLE II (*Continued*)

Comp. No.	IR (cm^{-1})	^{1}HNMR (ppm)
17b	3300-3200 (NH_2)	3.8 (brs, 2H, NH_2), 7.0-8.3 (m, 16H, ArH).
19a	3400 (OH enolic) 3000-2800 (NH)	3.5 (d, 1H, pyridine H-3), 4.1 (m, 1H, pyridine H-4), 6.1 (d, 1H, pyridine H-5), 7.2-8.2 (m, 10H, ArH), 11.7 (s, 1H, NH).
19b	3400 (OH enolic), 3000-2800 (NH)	3.4 (d, 1H, pyridine H-3), 4.1 (m, 1H, pyridine H-4), 6.1 (d, 1H, pyridine H-5), 7.2-8.1 (m, 15H, ArH), 11.4 (s, 1H, NH).
23	3250 (NH), 2200 (CN)	7.7-8.2 (m, 10H, ArH, pyridobenzothiazole H-3 and imino NH).
25	3300-2900 (NH_2), 2200 (CN)	7.1 (m, 2H, benzimidazole H-5 and H-6), 7.4 (m, 2H, pyridobenzimidazole H-5 and H-6), 7.6 (m, 2H, benzimidazole H-4 and H-7), 7.9 (q, 1H, pyridobenzimidazole H-4), 8.6 (q, 1H, pyridobenzimidazole H-7), 8.8 (s, 1H, pyridine H-2).

under the same experimental conditions used for the benzothiazole derivative affording 2-(3,4-dihydro-2-hydroxypyrid-3-yl)benzimidazoles (19a,b). Structure (19) was given based on elemental, IR, ^{1}HNMR and mass spectral data. Thus, the ^{1}HNMR of (19a) revealed an aliphatic proton patterns as two doublets at δ 3.5 and 6.1 ppm and a multiplet at δ 4.1 ppm integrated each to one proton and assigned to the dihydropyridine H-3, H-5 and H-4, respectively. Moreover their IR data showed an OH absorption at σ 3400 cm^{-1} and the characteristic benzimidazole imino ring absorption at 3000–2800 cm^{-1}.

The formation of both (17) and (19) is assumed to proceed via the intermediacy of the Micheal adduct (15) which reacts with ammonia with subsequent cyclization to afford the 2-iminodihydropyridine intermediate (16). The latter behaves differently in each case: with benzothiazoles, it undergoes oxidation under the reaction conditions to afford the isolable products (17) while with benzimidazoles it tautomerizes to the 2-imino-dihydropyridine (18) followed by hydrolysis to form the final isolable benzimidazolyl hydroxypyridines (19). A similar assumption regarding the effect of inter and intra hydrogen bonding in the course of the reactions involving benzimidazoles has been recently reported by us.[5]

In addition, 2-cyanomethylbenzothiazole was allowed to react with cinnamaldehyde in presence of acetic acid as a catalyst. The reaction occurred readily affording an excellent yield of the cinnamylidene derivative (20a) which was previously obtained on conducting the reaction in presence of piperidine as a catalyst.[5]



Scheme II

2-cyanomethylbenzimidazole reacted readily with cinnamaldehyde in the presence of acetic acid catalyst to afford the ylidene derivative (20b) rather than the imminium ylide which was obtained on using piperidine as a catalyst.[5]

On applying the above mentioned reaction to derivative (20b), the pyrido[1,6-a]benzimidazole (21) was obtained in a satisfactory yield. The MS spectrum of (21) showed a molecular formula $C_{18}H_{11}N_3$ ($m/z = 269$) which was compatible with the given structure. The IR spectrum showed the absence of the benzimidazole ring NH absorption which is usually detected for unsubstituted NH benzimidazoles.

It is assumed that product (21) was formed via intra Micheal addition envolving the benzimidazole ring NH as a nucleophile to afford the dihydropyrido[1,6-a]benzimidazole intermediate which was oxidized under the reaction conditions to the final isolable product; similar dihydropyridobenzimidazole oxidation has been previously reported.[9]

The reaction of (1a,b) towards triethylorthoformate was also investigated. When 2-cyanomethylbenzothiazole was boiled under reflux with triethylorthoformate, a bright yellow product precipitated, having a molecular formula $C_{19}H_{10}N_4S_2$ ($m/z = 358$). Its ^{1}HNMR revealed the presence of a multiplet at δ 7.7–8.2 ppm which integrated to 10 protons. Its IR spectrum showed a CN and an NH group absorptions at 2200 and 3250 cm^{-1}, respectively. These data along with the elemental analysis could be interpreted for the pyrido[1,6-b]benzothiazole structure (23).

When the same reaction was applied to 2-cyanomethylbenzimidazole a bright yellow product was also obtained with a relatively high melting point and mass spectral data confirming the incorporation of 2 moles of benzimidazole. The ^{1}HNMR spectrum of this product showed the aromatic protons signals, a singlet at δ 8.8 ppm integrated to one proton, not D_2O exchangeable. The IR spectrum revealed an amino group absorption at σ 3300–2900 cm^{-1}. Based on these data, the isomeric structure (25) was established for the reaction product.

The formation of compounds (25) and (23) could be postulated to proceed via the ylidene bis intermediates (24) and (22), respectively.

EXPERIMENTAL

All mp's were uncorrected. The IR spectra were recorded in KBr with a Pye-Unicam sp-1000 spectrometer. The ^{1}HNMR spectra were run on a Varian EM 390 (90 MHz) or Gemini-200 spectrometers using TMS as an internal reference. The mass spectra were recorded at 70 ev with a Varian MAT 311 A mass spectrometer. Elemental analyses were performed by the Central Service Laboratory in the National Research Centre.

3-Aroylamino-3-mercapto-2-(benzothiazol-2-yl)acrylonitrile (2a,b). General procedure. A solution of (1a) (0.01 mole, 1.74 g) in dry dioxane (30 ml) was treated with aroylisothiocyanate (aroyl = benzoyl, furoyl) (0.01 mole) (prepared according to reported methods).[10,11] The reaction mixture was stirred at room temperature (25°C) for 4–5 hours. The solution was then poured onto water, the resulting solid was filtered off and washed thoroughly with water followed by crystallization from the proper solvent (cf. Table I).

3-Aroylamino-3-methylmercapto-2-(benzothiazol-2-yl)acrylonitrile (3a,b). General procedure. A solution of each of (2a,b) (0.01 mole) in dry dimethyl sulfoxide (20 ml) was treated with sodium hydride (0.01 mole, 0.24 g) and stirred for 2 hours. Methyl iodide (0.01 mole, 1.42 g) in 5 ml dry dimethyl sulphoxide) was then added dropwise over a period of 15 minutes and the mixture was then stirred for further 6 hours. The solution was then poured onto water, the resulting solid product was filtered off, washed with water and crystallized from the proper solvent (cf. Table I).

2-(2-Aryl-4-methylmercapto-6-oxo-1H-pyrimidin-5-yl)benzothiazole (5a,b). General procedure. A solution of each of (3a,b) (0.01 mole) in dry pyridine (30 ml) in presence of sodium methoxide (0.01 mole) was boiled under reflux for 6 hours. The solution was then poured onto water, the resulting solid product was filtered off, washed with dilute hydrochloric acid then thoroughly with water and crystallized from the proper solvent (cf. Table I).

6-Amino-3-phenylpyrimido[5',4':4,5]pyrimido[6,1-b]benzothiazol-1-one (6). A mixture of (5a) (0.01 mole, 3.5 g) and guanidine sulfate (0.01 mole, 2.14 g) in dry pyridine (30 ml) was boiled under reflux for 6 hours in presence of sodium methoxide (0.01 mole). The solution was cooled, poured onto water, the precipitate formed was washed first with dilute hydrochloric acid then with water and crystallized from pyridine affording 1.9 g (55% yield) of brown crystals, m.p. 278°C

Anal. Calcd. for $C_{18}H_{11}N_5OS$ (345.377): C, 62.60; H, 3.21; N, 20.28; S, 9.28.

Found: C, 62.39; H, 2.95; N, 20.09; S, 8.95.

2-(3,5-Diaminopyrazol-4-yl)benzothiazole (8). Compounds (2a,b) (0.01 mole) were refluxed each with hydrazine hydrate 99% (0.03 mole, 1 g) in dioxane (20 ml) for 6 hours. The reaction mixture was then concentrated, cooled and the precipitate formed was filtered off and crystallized from dioxane to give 1.15 g (50% yield) of yellow crystals, m.p. 200°C

Anal. Calcd. for $C_{10}H_9N_5S$ (231.27): C, 51.93; H, 3.92; N, 30.28; S, 13.86.

Found: C, 51.58; H, 3.71; N, 29.95; S, 13.50.

α-Carboethoxy-2-cyanomethylazoles (9,11) and 1-carboethoxy-2-cyanomethylbenzimidazole (12). General procedure. Compounds (10a,b) (0.01 mole) were treated each with an equimolecular amount of ethyl chloroformate (1.1 g) in dry dioxane (30 ml) in the presence of triethylamine (0.01 mole, 1.0 g) at room temperature (25°C) for 10 hours with stirring. The solution was then poured onto water, the resulting solid product was filtered off, washed with water and crystallized from the proper solvent (cf. Table I). In case of (1b), the reaction afforded two products (11) and (12) which were separated by fractional crystallization from dioxane where compound (11) precipitated first.

2,4-Diamino-5-(benzothiazol-2-yl)-6-hydroxypyrimidine (10) and 1-amino-3-hydroxy-4-cyanopyrimido[1,6-a]benzimidazole (13). General procedure. A solution of (9 or 11) (0.01 mole) in dry pyridine (50 ml) was treated each with sodium methoxide (0.01 mole) and guanidine sulfate (0.01 mole, 2.14 g). The reaction mixture was refluxed for 10 hours. The solution was then poured onto water, the resulting solid product was filtered off, washed with water and crystallized from the proper solvent to afford compounds (10) and (13), respectively.

4,6-Diaryl-3-(benzothiazol-2-yl)-2-aminopyridine (17a,b) and 4,6-Diaryl-3-(benzimidazol-2-yl)-2-hydroxy-3,4-dihydropyridine (19a,b). General procedure. Compounds (1a,b) (0.01 mole) were each boiled under reflux with an equimolecular amount of each of the propenones (14a,b) in ethanol (35 ml) in presence of ammonium acetate (0.08 mole, 6.1 g) for 8 hours. The solution was concentrated and left to cool. The solid formed was collected and crystallized from the proper solvent (cf. Table I).

M.S. (*m*/*z*) of (17b): 447.

1-Cyano-1-(benzoazol-2-yl)-4-phenylbuta-1,3-diene (20a,b). General procedure. A solution of (1a,b) (0.01 mole) in methanol (30 ml) was treated each with cinnamaldehyde (0.01 mole, 1.3 g) in presence of acetic acid (4 drops) at 25°C with stirring for 2 hours. The resulting solid product was filtered off and crystallized from the proper solvent (cf. Table I).

1-Phenyl-4-cyanopyrido[1,6-a]benzimidazole (21). Compound (20b) (0.01 mole, 2.7 g) was boiled under reflux in pyridine (20 ml) for 6 hours. The reaction mixure was concentrated, cooled and water was added till precipitation commenced. The solid product formed was filtered off and crystallized from dioxane affording 1.7 g (63% yield) of yellow crystals m.p. 251–53°C.

Anal. Calcd. for $C_{18}H_{11}N_3$ (269.29): C, 80.27; H, 4.11; N, 15.60.

Found: C, 79.99; H, 3.86; N, 15.25.

M.S. (*m*/*z* = 269).

2-(Benzothiazol-2-yl)-4-cyano-1-iminopyrido[1,6-b]benzothiazole (23) and 2-(Benzimidazol-2-yl)-4-cyano-3-aminopyrido[1,6-a]benzimidazole (25). General procedure. Compounds (1a,b) (0.01 mole) were boiled each under reflux with triethylorthoformate (0.01 mole, 1.48 g) in ethanol (25 ml) for 4 hours. The reaction mixture was left to cool and the solid product formed was filtered off and crystallized from the suitable solvent (cf. Table I).

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